Direct observation of phase transformation in MnAl(C) alloys

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ABSTRACT

The phase transformation in two modes, including both displacive and massive growth of τ-phase from ε-MnAl(C), was *in situ* observed. Temperature dependence of magnetization curves of MnAl(C) under magnetic field were employed for the first time to determine the triggering temperatures of different phase transformation modes. The displacive growth of ε→τ in MnAl(MnAlC) occurs at temperatures below 650 K(766 K), above which both modes coexist. One third or less of the ε-phase can be transformed into τ via displacive mode while the remaining two thirds or more via massive mode. Most large τ-grains formed via massive mode are actually containing a large number of well-distributed τ-nanocrystallline formed via displacive mode. The typical massive growth rate of the τ-phase is 8-60 nm/s, while the displacive growth rate is quite low. The doping of C to MnAl prevents the growth of ε-phase along the basal plane and thus increases the activation temperatures of the phase transformations and the decomposition of τ-phase. Pure τ-phase with highest magnetizations up to 118.3 Am^2/kg was obtained. No decomposition was observed in τ-MnAl and τ-MnAl(C) after long-time annealing at selected temperatures, which are crucial in preventing the metastable τ phase from decomposition. These results provide a more complete understanding of the ε→τ phase transformations and thus facilitate the development of high-performance MnAl-based magnets.

Keywords:

Phase transformation; Magnetic properties; Diffusion growth; MnAl; Decomposition.

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1. Introduction

The $L1_0$ structured τ-phase MnAl, usually prepared by annealing the hexagonal ε-phase MnAl at moderate temperatures, is attracting increasing research interests for its low cost and high performance as promising rare earth (RE) free magnets [1-6]. The metastable nature of τ-MnAl is a barrier to the preparation of pure ferromagnetic τ-phase for which decomposes during high temperature annealing necessary to the ε→τ phase transformation (PT) [2]. The doping of C to MnAl can to some extent improve the stability of τ-MnAl [2, 7], but the mechanism remains unknown. Full understanding of the PT is vital to overcome the above barriers and to develop high performance MnAl–based magnets.

The PT of ε→τ in MnAl has been studied by several groups over decades but there are still controversial and unclear issues [8-12]. Early x-ray diffraction (XRD) studies showed that the hexagonal-close-packed ε-phase transforms into an orthorhombic (ε′) phase by an ordering reaction first, and then to the metastable ferromagnetic face-centered-tetragonal τ-phase by a diffusionless displacive shear reaction [8]. According to Broek, the displacive mode of the ε→τ PT follows the sequence ε→ε'→polytypes→τ, where the τ-phase was assumed to nucleate in ε'-domain [9]. However, the later metallographic studies indicated that the ε→τ PT occurred via a compositionally invariant, diffusional transformation akin to the so-called massive transformation rather than a displacive or martensitic transformation [10]. The coexistence of the diffusional massive and the displacive shear modes during the formation of τ-MnAl had also been reported [8]. A hybrid displacive-diffusional mechanism involving the motion of partial dislocations that act as transformation dislocations and concomitant short-range diffusion has been observed in recent years [11]. The previous studies showed us a complex and an unclear nature of the PT in MnAl. Different PT mechanisms have been proposed based on different samples but the relationship between these mechanisms and the factors that triggering different mechanisms were not clear due to the following reasons.

Most previous transmission electron microscopy (TEM) observations on the ε→τ PT were carried out on postmortem samples, in which the ε- and τ-phases were formed prior to the room temperature examinations by TEM [8-10, 12]. The details of the ε→τ PT occurred at high temperatures before observation are restored indirectly through reasoning and imagination. However, it is difficult to imagine the formation sequence of different τ-phase grains observed at the same time, leaving losing or incomplete details of the process. Wiezorek et al. reported some details of the dynamic sequences of PT during the *in situ* TEM heating experiments conducted at temperatures between 540-650 ℃, at which both the dominating massive ordering mode and the hybrid displacive-diffusional mode were observed [11]. The displacive mode usually occurs at lower temperatures while the massive mode dominates at high temperatures, but the exact temperature range is unknown.

Since the rate for ε→τ massive transformation is so fast that it usually completed within several tens of seconds to typically no more than 20 minutes, it is important to select proper time windows to capture the dynamic details by *in situ* TEM before the completion of the PT. A higher temperature may result in very fast PT so that we have no enough time for observation. A lower temperature may result in partial transformation by merely displacive mode rather than massive mode. In this work, we determined the dividing temperature between displacive mode and massive mode by using magnetic measurement, based on which the temperature with medium rate of ε→τ was selected for *in situ* TEM to make sure that we have enough time to capture more details of the transformation. Moreover, it is known that excess Mn and/or carbon addition are effective in stabilizing the structure of the metastable τ-MnAl but the mechanism is still unclear. The purpose of the present study is to unravel some of the unclear controversial issues regarding the displacive/massive transformations and the factors that controlling the morphology and structure of the resultant phases.

The metastable nature of both ε and τ phase of MnAl makes it difficult to prepare high purity τ phase for which might decompose before the full transformation of ε to τ at elevated temperatures. The fraction of ferromagnetic τ-phase in the samples is crucial for the development high performance MnAl-based magnets. High fraction of τ-phase indicates high saturate magnetization (M_s) and thus high potential for applications. The room

temperature M_s of MnAl-based magnets prepared by the traditional two-step process, including melting and annealing steps, was reported to be ~73 Am^2/kg at 2 T [13], ~82 Am^2/kg at 2 T [6], 94 Am^2/kg at 3 T [14], and 100 Am^2/kg at 14 T [15]. The room temperature M_s of samples prepared by one step process, including one-step strip casting technique and direct drop synthesis method, has been reported recently to be 114 Am^2/kg at 5 T [3], and 117 Am^2/kg at 9 T [5], respectively. In this work, the M_s of our samples of MnAlC and MnAl prepared by traditional two-step process reached up to ~114 Am^2/kg at 4 T, and 118.3 Am^2/kg at 8.5 T, respectively, indicating the effectiveness of our work in controlling the PT.

2. Experimental procedure

The alloys with nominal composition of $Mn_{54}Al_{46}$ and $Mn_{54}Al_{46}C_{2.44}$, hereafter denoted by MnAl and MnAlC, were produced from manganese (purity 99.95%) and aluminum (purity 99.999%) pieces with a high-frequency vacuum induction furnace in argon atmosphere (purity 99.999%). The melt was cast in an alumina mold. The compositional deviation due to the volatility of Mn in the molten state was minimized by maintaining the molten state within 3 minutes. To increase the homogeneity, the as-cast alloys were annealed for 24 hours at 1150 ℃ (where the high temperature ε-phase is stable), and then quenched into water to prevent the decomposition of the ε-phase into the equilibrium phases, i.e., γ_2+β-phases, and the formation of the τ-phase. After that, the ε-phase was annealed at 773 K for varied time intervals to attain τ-phase.

The structure of the samples was characterized by XRD with Cu-K_α radiation. The morphology of a selected piece of ε-MnAlC was observed by using scanning electron microscopy (SEM). The PT of the ε-$Mn_{54}Al_{46}C_{2.44}$ at 773 K was *in situ* studied using a JEOL 200CX TEM. Thin foils of the as-quenched ε-phase for TEM observations were prepared by using a focused ion beam (FIB) workstation. The magnetic properties were measured using a Quantum Design physical property measurement system (PPMS).

3. Results and discussion

3. 1 Phase transformation probed by XRD

The XRD patterns of both MnAl and MnAlC alloys after 1150 ℃-homogenization followed by water quenching could be indexed with single ε-phase, as shown in Fig. 1(a). Both ε-MnAl and ε-MnAlC, when heated at 500℃, transformed into pure τ-phase in 15 minutes. Trace amount of γ_2+β phases precipitate from τ-MnAl after heating for 25 min, indicating decomposition of τ-MnAl under prolonged heating time at 500 ℃, owing to the lower decomposition temperature of τ-MnAl as determined below by magnetic measurements. However, no decomposition was found in τ-MnAlC after heating for 40 minutes, indicating structural stabilization effect of carbon in the lattices. Both ε- and τ- phases exist in MnAlC heated for 10 minutes, indicating incomplete PT in this stage. The time windows for the precipitation of different phases during the ε→τ PT at 500 ℃ are important for guiding the following *in situ* TEM heating and observations.

Detailed investigations showed that the diffraction peaks of the (0002) plane in ε-MnAlC and the (111) plane in τ-MnAlC shift slightly to lower angles in the carbon doped samples, indicating larger lattice parameters in MnAlC than that in MnAl. It is interesting that the ε-MnAlC shows a much stronger diffraction peak of (0002) planes and very weak diffraction of the other planes. For comparison, the x-ray diffraction intensities of different planes in ε-MnAl do not vary much. According to the Scherrer equation, the intensity of x-ray diffraction is largely dependent on the crystalline dimensions or size in the samples. Therefore the strong diffraction peak of the (0002) plane in ε-MnAlC was ascribed to the much larger dimension of the ε-phase along the c-axis than that along directions perpendicular to the c-axis. The comparable diffraction intensities of different peaks in ε-MnAl indicate comparable dimensions of the ε-phase in different directions. It seems the carbon atoms in ε-MnAl lattices hinder the growth of ε-phase along the basal plane and thus the dimension of atomic long-range ordering is reduced. The preferential growth was further proved by SEM observations on a selected piece of water quenched MnAlC as shown in Fig. 1(b), in which a number of cleavage fractures were observed. The mechanism

of such blocking effect of carbon on the long-range ordering along the basal plane in ε-MnAlC is not clear, but may related to the stabilization effect of carbon on the subsequent τ-phase transformed. Similar lamellar morphology was not observed in ε-MnAl.

3.2 Phase transformation probed by M-T curves

The reason for τ-MnAl decomposed while τ-MnAlC did not decompose at 773 K as shown in XRD patterns could be found in Fig. 2, which plots the temperature dependence of magnetization of the ε-MnAl and ε-MnAlC measured with increasing temperature (20 K/min) under an applied field of 2 Tesla. At temperatures above 750 K (838 K), the magnetization of MnAl (MnAlC) decreases quickly with increasing temperature, indicating decomposition of the ferromagnetic τ-phase. The annealing temperature of 773 K is higher (lower) than the decomposition temperature of τ-MnAl (τ-MnAlC). As a result, τ-MnAl decomposed while τ-MnAlC did not decompose after prolonged heating time.

The magnetization of both samples decrease with increasing temperature from 300 K, owing to the thermal effect. However, the downward tendency of M reversed at temperatures above 510 K and 540 K for MnAl and MnAlC, respectively, indicating occurrence of PT from ε/ε' to ferromagnetic τ-phase. The magnetizations of MnAl and MnAlC do not vary too much at 510-650 K and 540-766 K, respectively, indicating occurrence of additional magnetization due to PT in compensation of the thermal driven magnetization loss in this temperature range. The PT during this stage was slow and was ascribed to the displacive PT, which is a low temperature diffusionless process involving co-operative shear movements of atoms on $(001)_{\varepsilon'}$ along $[010]_{\varepsilon'}$ that produces the final tetragonal lattice of τ.

A sharp magnetization increase was observed at temperatures above 650 K and 766 K for MnAl and MnAlC, respectively, indicating occurrence of high-rate PT in the samples. The PT during this stage was fast and was ascribed to the massive mode. This result is in good agreements with the XRD results as mentioned above and the TEM results as discussed below.

It is known that the addition of a small amount of carbon (within the solubility limits) could stabilize the τ-phase of MnAl as evidenced that τ-MnAl tends to decompose into γ_2+β-phase while τ-MnAlC does not decompose even if the heat treatment temperature and time are the same. However, the mechanisms for such stabilizing effect are still not clear. Fig. 2 shows that the minimal temperature (766 K) for activation of massive growth of τ-MnAlC is higher than the decomposing temperature (750 K) of τ-MnAl. As a result, it is not strange to observe the decomposition of τ-MnAl if we want to obtain τ-MnAlC by the same heating process. In fact, carbon not only increases the decomposition temperature of τ-phase, but also increases the activation temperatures for both displacive and massive transformations of ε-phase, as shown in Fig. 2. It seems that carbon increased the energy barriers of the PT and decomposition.

3.3 Short-range displacive mode probed by *in situ* TEM

The *in situ* heating TEM observations on the PT of the ε-MnAlC within the initial 10 minutes are shown in Fig. 3. The parent ε-MnAlC shows continuous bright contrast before heating, as seen in Fig. 3(a), in which traces of impurities (marked with I) could also be observed. It had been proved that the water-quenched materials, which from X-ray analysis was expected to be pure hexagonal ε-phase, already contains numerous small nuclei of the ordered orthorhombic ε'-phase that are 4-10 nm in size, which grows to 30-40 nm upon heating to 450 ℃ [9].

The ε→ε' process is one of ordering in the close-packed *c*-plane of the sixfold symmetry hcp structure. The reduction in symmetry to twofold caused by the ordering results in the orthorhombic unit cell of the ε'-phase. Therefore, there are three symmetry-equivalent variants for ε' in one original ε crystal. The orientation relationships between the ε-phase and the three variants of ε' precipitates are as follow [11]:

ε_1': (0001) ε//(001) ε_1' and [11 $\bar{2}$0] ε//[010] ε_1'

ε_2': (0001) ε//(001) ε_2' and [1 $\bar{2}$10] ε//[010] ε_2'

ε_3': (0001) ε//(001) ε_3' and [$\bar{2}$110] ε//[010] ε_3'

The ε+ε' phase, when heated for several minutes, starts to precipitate small τ-grains, as shown in Fig. 3(b). Fig. 3 (d, e) show that the small τ-grains embedded in the ε+ε' matrix grows slowly to a maximum size of about 40 nm with increasing heating time. It is interesting that these evenly distributed τ-grains could not grow further when its size reached ~40 nm, which is the size of a ε' grain as observed previously [9]. The distribution of isolated island-like τ-grains embedded in ε-matrix is quite different from massive transformation characteristics, but could be well explained by displacive mode.

Although there are three variants of ε', only one type of partial dislocation can shear one of the three possible ε'-phase variants that may be produced in a given ε-grain into the $L1_0$ structure with the required correct ordering of atoms. If several partial dislocation glide on every other close-packed plane of the parent phase in which there are two or three variants of ε', the resulting structure will not be $L1_0$. Hence, in a given ε-phase grain, one "correct" variant and two obstacle variants of the ε'-phase exist [11]. The two obstacle ε' variants neighboring to the correct one have largely restrained the maximal size of τ-grain formed by displacive mode. The τ-phase grows through the motion of the partial dislocations along the close-packed plane. When a dislocation encounters the obstacle variants of ε_2' and ε_3', its motion is obstructed. The ε_2' and ε_3' variants have to reorder to become τ-phase. However, motion of a partial dislocation group with a Burgers vector that transforms ε_1' into the correct $L1_0$ order would not lead to the formation of the $L1_0$ structure from ε_2' and ε_3', but to a higher energy structure which was not observed. The strain originating from the transformation of ε_1' to τ and obstacle effect of ε_2' and ε_3' would hinder the subsequent growth of τ-grains. There are also some larger τ-islands that were actually composed of two or three connected smaller τ-grains, owing to the presence of neighboring ε' variants of the same type. Fig. 3(d, e) shows that the region for τ-phase with dark contrast accounts approximately one third of the total area in view. This further proved that only one of the three variants was transformed into τ-phase by displacive mode. More evidence for this 1/3 phenomenon could be found in the following magnetic measurements. The small τ-gain nuclei are also difficult to propagate to the neighboring ε' grains through the boundaries via shear mode due to incoherent interfaces and increasing shear strains.

In fact, it is difficult to observe the transformation sequence of these three ε' variants by postmortem TEM because we could not distinguish the τ formed by different variants. Our *in situ* TEM observations provide time resolution for these transformations. Besides many small τ-grains formed in the parent ε-grains through shear mode (marked as τ_s), a much larger τ-grain with size up to 180 nm nucleated at grain boundary has also been observed as marked with τ_m in Fig. 3 (c). The τ-phase grown at grain boundaries has been proved to be crucial for the massive mode of PT [11, 12].

3.4 Long-range massive mode probed by *in situ* TEM

The massive transformation is generally defined as a compositionally invariant nucleation and growth process involving a change in crystal structure and/or degree of long-range order. The growth of the massive τ-phase in MnAl is accomplished with the migration of incoherent heterophase interfaces by essentially random atomic attachment across the growth interface and is associated with the genesis of characteristic defect such as stacking faults, microtwins, and antiphase boundaries in the τ-phase product [11]. Since the shear mode itself could not transform all the ε-phase into τ, a diffusion controlled reordering process must occur for all the three ε' variants were transformed into τ finally, but it is not clear when it takes place. Two possible mechanisms for (ε_2'+ε_3')→τ were proposed in the previous work. It might occur in the bulk as a consequence of coarsening of ε_1'. A second possibility is that reordering occurs near the core of the transformation dislocations where diffusion is enhanced. Our work shows that the ε_2'+ε_3' transformed into τ mainly through thermally activated massive diffusional process. As mentioned above, the grain size of τ formed via coarsening of ε_1' usually is no larger than 40 nm, thus the enhancing diffusion in the ε_1'→τ transformation dislocations should be very limited. For comparison, the growth rate and the maximal grain size of the τ-phase produced via diffusional process is much

higher and larger than that formed via displacive mode.

Fig. 4(a,b,c) shows the growth process of the τ-phase via massive mode. More details could be found in the supplementary movie 1. These *in situ* videos and micrographs captured a number of unique features of τ-phase formation in the MnAlC alloys.

First, the small τ_s-grains formed via displacive transformation from ε_1' make almost no change during the massive transformation of the surrounding ε/ε' to τ_m, resulting in a structure of τ_s embedded in τ_m, as seen in Fig. 4(a-c). It should be noted that the size of the τ_s-grains might vary a little with massive transformation rate and temperature. Since the τ_s-grains near the massive transformation frontiers have no enough time for a fully coarsening of τ_s via displacive mode, the grain size of τ_s thus should be smaller than those far from the massive transformation frontiers, as proved by the smaller grain size of τ_s in Fig. 4 than that in Fig. 3(d,e). Of course, the obscure boundaries between τ_m and τ_s might also result in a seemingly smaller τ_s size. Usually, the thermal activated massive transformation is accelerated with increasing temperature, a fast enough massive transformation might transform all the samples into τ in several seconds and give little time for τ_s to grow and for us to observe by *in situ* TEM. It is also possible for the metastable τ_s to be consumed by τ_m through diffusional process at higher temperatures. The τ-phase can form via massive mode without prior ε→ε' ordering at high enough temperatures [11]. The annealing at 773 K provides medium massive transformation rate and thus both modes are *in situ* observed.

Second, the rate of the propagation of the massive transformation front ranges from 8 nm/s to 60 nm/s, depending on the front shape. The propagation rates of the inter-phase interface with arc-shape, straight shape, and sharp-angle tip of τ_m are ~8 nm/s, ~10 nm/s, and ~16 nm/s, respectively. The ε/ε' phase in the sharp angle in-between two τ_m grains transforms at a rate up to 60 nm/s, which slows down quickly when the sharp angle become obtuse due to ε/ε'→τ transformations. It should be noted that the high rate area is very limited while most linear growth rates are falling in the range 8-16 nm/s. Yanar et al. analyzed the growth kinetics of the τ phase in the Mn-Al-C alloys using modified Burke-Turnbull equation and postmortem TEM, yielding a linear growth velocity of ~1 μm/s [12], which is much larger than what we observed by *in situ* TEM. Yanar et al. determined the growth rate by dividing the growth distance by the estimated time of growth, while the growth distance was calculated by averaging maximum size measured in five τ colonies [12]. We speculate that one τ colony in the postmortem TEM sample might contain many τ grains grown from different nuclei at the same time, thus the growth distance might be overestimated. In fact, our in situ TEM studies showed that there are many τ grains grew from many different τ nuclei distributed in the sample. If several τ grains from different nuclei met together and grew into one τ colony, it is difficult to distinguish them by postmortem TEM observations. By applying the modified Burke-Turnbull equation and the average growth rate observed by our *in situ* TEM, the activation energy for diffusional growth in MnAlC is estimated to be 182.5 kJ/mol, which falls in the range of that reported by Lu et.al but higher than that estimated by Yanar et al. [12, 16].

Third, new τ grains tend to grow along the boundaries of the as-formed τ_m grains. The growth of one τ_m is hindered when encountered another τ_m–grain. Stacking faults during the transformation are usually accumulated in the grain boundaries between the τ_m grains. The prominent facets that appear in the growing τ phase colonies are incoherent interfaces with no systematic orientation relationship with the parent ε/ε' phase.

The magnetizations of MnAlC after fully PT at different temperatures through different modes further proved that one third of the ε-phase in maximal could transform into τ via displacive mode. Fig. 4(d) shows the room temperature magnetic hysteresis loops of the ε-MnAlC after 13-hour annealing in 4 T. The field-assisted long-time annealing provides fully transformation of τ-phase in ε-MnAlC at 623 K via displacive mode and at 773 K via both modes. The saturation magnetization (35 Am^2/kg) of the 623 K annealed sample is one third of that (~105 Am^2/kg) in the 773 K annealed sample. This proved that only one of three possible ε' variants were transformed via displacive mode into τ-phase at 623 K, a temperature at which massive transformation is impossible. This is in good agreement with the above TEM observations, in which τ_s grains covered approximately one third of the field

in view. The Curie temperature for our τ-MnAl and τ-MnAlC is measured (not shown here) to be 630 K and 550 K, respectively. The addition of carbon significantly decreased the Curie temperature of τ-MnAl.

It was usually accepted that the massive transformation of the τ phase involves a nucleation and growth process, with nucleation occurring almost exclusively heterogeneously along the prior-ε-phase boundaries [11]. Fig. 3(c) shows the nucleation process of this case. We have also observed new τ_m nucleation process at the $\varepsilon/\tau_{m1}/\tau_{m2}$ triple junctions, as typically shown in Fig. 5. When two grains of τ_{m1} and τ_{m2} met during fast growth, a $\varepsilon/\tau_{m1}/\tau_{m2}$ triple junction was formed, as shown in Fig. 5(a). Fig. 5(b, c, d) showed the precipitation and growth processes of the new τ-nuclei for massive transformations. More details about this process can be found in the supplementary movies 2.

3.5 Phase transformation fraction/rate probed by M-H/M-t curves

The magnetization of the samples is largely dependent on the fraction of nonmagnetic ε transformed into ferromagnetic τ. Fig. 6 shows the demagnetization curves of τ-MnAl and τ-MnAlC at 300 K. The magnetization of our τ-MnAlC and τ-MnAl reached up to ~114 Am^2/kg at 4 T, and 118.3 Am^2/kg at 8.5 T, respectively. The magnetization of our samples is higher than most previously reported values [3, 5, 6, 13-15], indicating higher fraction of the τ-phase in our samples.

The time dependence of magnetizations of ε-MnAl at 573 K and 673 K are shown in the inset of Fig. 6, which to some extent shows the PT rate/fraction of ε→τ with time. The magnetization of ε-MnAl becomes saturated when heated at 673 K for 15 minutes, indicating full transformation of the ε to τ phase. However, no saturation was observed in ε-MnAl when heated at 573 K for more than 12 hours, indicating very slow PT rate at this temperature. As mentioned above, for ε-MnAl, the displacive mode acts at 573 K while massive mode dominates the PT at 673 K. Fast transformation rate is the characteristic of the massive transformation. The low transformation rate of displacive mode is ascribed to the obstacle effect of ε_2' and ε_3' to the shearing process of ε_1' variants. In fact, the coarsening rate of τ_s is observed to be very slow in our *in situ* TEM experiments, even the temperature is as high as 773 K, as partly shown in Fig. 3.

4. Conclusions

Based on the results of the current studies including XRD analysis, *in situ* TEM observations, and magnetic measurements on the MnAl and MnAlC alloys, a clear and more complete understanding of the ε→τ PT has been developed. The PT modes are mainly selected by temperatures. Only the displacive mode exists in the low temperature region, 510-650K for MnAl and 540-766 K for MnAlC. The displacive mode and the massive mode coexist at higher temperatures, while the weight of massive mode increases with increasing temperature. The τ-MnAl and τ-MnAlC start to decompose at temperatures above 750 K and 838 K, respectively. Only one third or less of the ε-phase can be transformed into τ via displacive mode and the remaining two thirds or more via massive mode. The typical growth rate of the τ-MnAlC grains at 773 K is 8-60 nm/s. Pure ferromagnetic τ-MnAl without any addition of stabilizers was prepared by controlling the temperature and heating time. Temperature (or time) dependence of magnetization measurements under magnetic fields is developed to determine the activation temperature (or PT rate) of both displacive and massive PT of ε→τ in MnAl-based magnets.

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Appendix A. Supplementary movie 1: Massive growth of τ-phase in ε-MnAlC.

Appendix B. Supplementary movie 2: Nucleation and growth of a grain of τ-phase in ε-MnAlC.

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Figures:

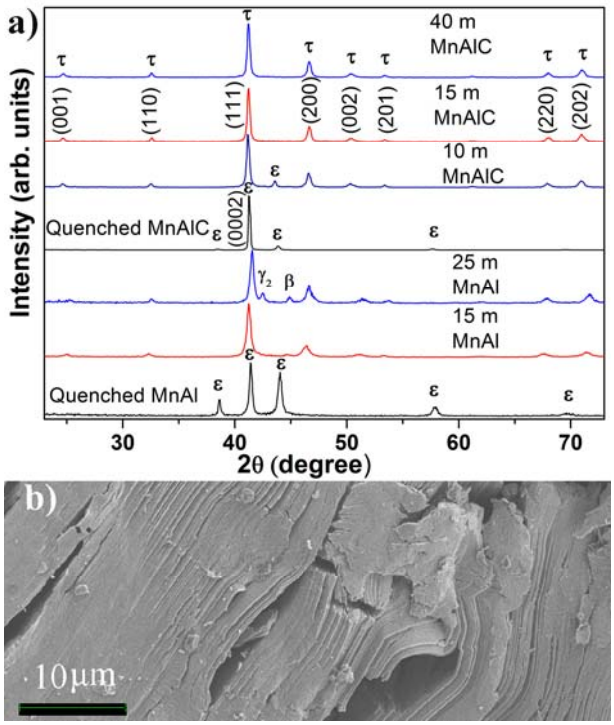

Fig. 1 a) XRD patterns. The water-quenched MnAl and MnAlC are single ε-phase. The diffraction intensity of (0002) in ε-MnAlC is much higher than that of the other planes. Single τ-phase was obtained in MnAl annealed for 15 minutes and in MnAlC annealed for 15 and 40 minutes. A small fraction of τ-phase in MnAl decomposed to γ_2+β-phases when annealed for 25 minutes. The MnAlC annealed for 10 minutes is composed of ε+τ-phases. b) Cleavage fractures observed by SEM indicate preferential growth of the water quenched MnAlC.

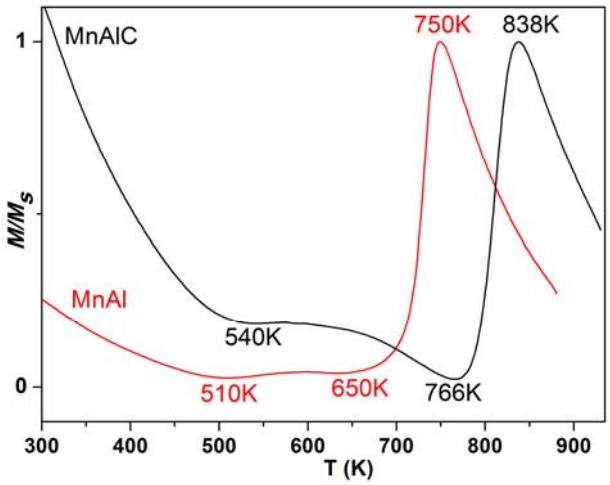

Fig. 2 Normalized M-T curves of ε-MnAl/ε-MnAlC under 2 T. The massive phase transformation is thermally activated at temperatures above 650 K/766 K, below which the displacive mode acts. The ferromagnetic τ-MnAl and τ-MnAlC decompose at temperatures above 750 K and 838 K, respectively.

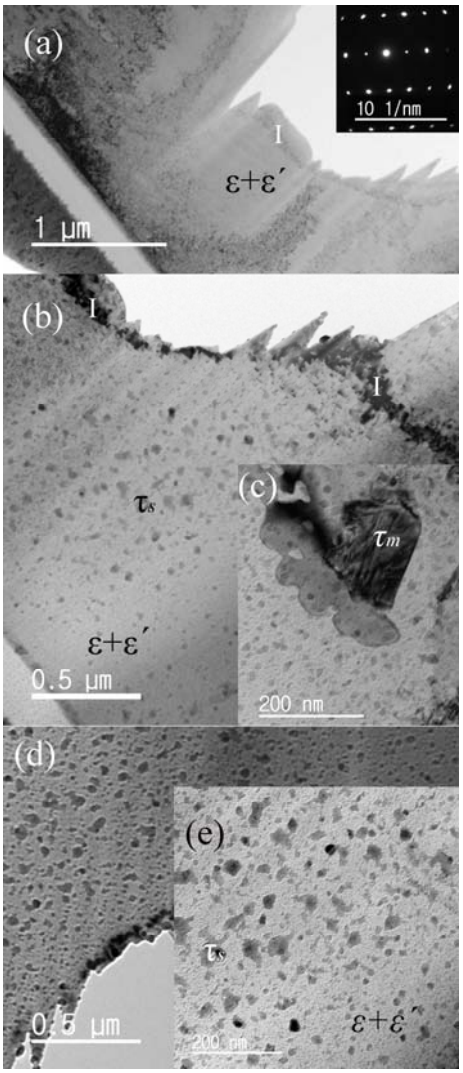

Fig. 3. TEM images: (a) the parent ε+ε' phase show continuous bright contrast with the electron diffraction patterns shown as inset. With increasing annealing time, τ-phase was formed via (b) displacive shear mode denoted as τ_s and (c) massive diffusion mode denoted as τ_m; (d, e) The τ_s-grains grows up to 40 nm slowly with time and covers ~1/3 of the field in view. Impurities (marked as I) was observed to accumulate in grain boundaries.

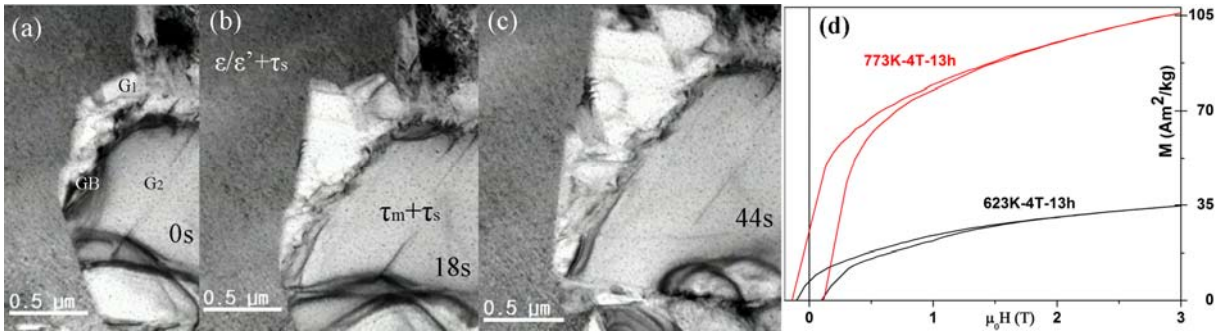

Fig. 4 Massive growth of τ_m-grains. (a) One τ-grain G1 hinders the growth of another τ-grain G2, producing grain boundaries GB with thickness of ~80 nm. (b) The τ_s-grains (formed via displacive mode) embedding in the parent ε/ε' phase were embedded in the matrix of growing τ_m-grains formed via massive mode. (c) The growth rate of τ_m is estimated based on the size of the grains and the time required reaching it. (d) Room temperature M-H plots of the ε-MnAlC after 13-hour annealing in 4 T. The saturate magnetization (35 Am^2/kg) of the 623 K annealed sample is one third of the magnetization (~105 Am^2/kg) in the 773 K annealed sample. This further proved that only one of three possible ε' variants were transformed through displacive mode into τ-phase at 623 K, a temperature at which massive transformation is impossible.

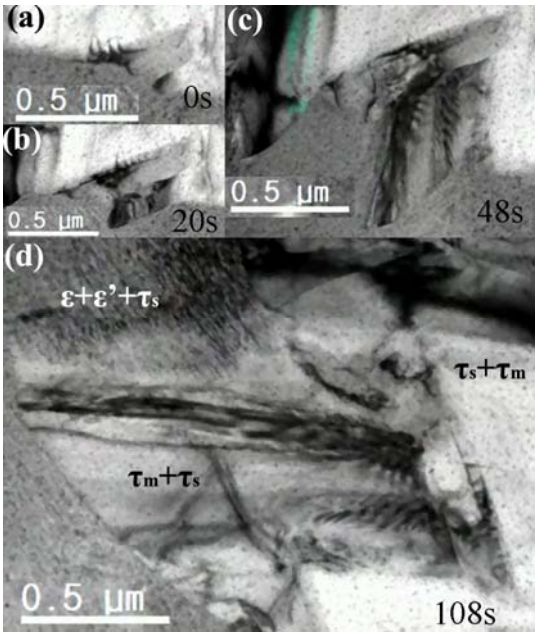

Fig. 5 *In situ* TEM images of the nucleation and growth of a τ_m grain. (a) a small τ_m grain is seen to nucleate from ε/ε' grain tip in conjunction with notched τ-grains. (b,c,d) TEM images of the nuclei after growth of 20s, 48s, and 108s, respectively.

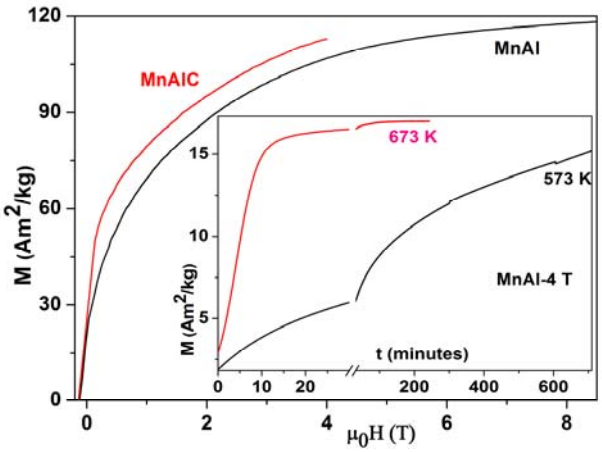

Fig. 6 Room temperature demagnetization curves of τ-MnAl and τ-MnAlC. The inset shows M-t plots of ε-MnAl during field-heating at 573 K and 673 K, respectively.